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CERAMIC COMPOSITION AND ARTICLE

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This invention relates to vitreous enamel resistor compositions which may be applied to and fired on a ceramic dielectric body to produce an electrical resistor, and resistors prepared therefrom.

Many attempts have been made heretofore to produce electrical resistors by applying an enamel containing an electrically conductive material on a ceramic insulator and firing the same to fuse and mature the enamel composition. Such previously produced resistors, although operative, were not commercially practicable since it was difficult to reproduce the same to a given resistance value.

It is an object of this invention to produce a vitreous enamel resistor composition that may be fired on a ceramic dielectric base to form an electrical resistance of readily reproducible resistance value.

It is another object of this invention to produce an improved vitreous enamel resistor composition.

It is a further object of this invention to produce an improved, extremely stable vitreous enamel electrical resistor.

Other objects of this invention will appear hereinafter.

The vitreous enamel resistor composition of this invention may be obtained by mixing with a vitreous frit or enamel finely divided palladium. The dry, finely divided mixture may be applied to a ceramic dielectric body and then fired to fuse the enamel frit and bond the palladium and frit to the dielectric.

The resistor compositions of this invention are preferably mixed with a vehicle and applied to a ceramic dielectric by brushing, spraying, printing, or screen stencil application, and fired at the fusing temperature of the glass frits contained therein to produce exceedingly stable resistor films with excellent resistor values between a few ohms to several megohms per square with excellent voltage and temperature coefficients and excellent reproducibility.

In order that the voltage and temperature coefficients of the resulting resistor element may be more readily adjusted and controlled, and so that the resistors may be more easily reproduced, it is preferred that a quantity of finely divided silver be included in the resistor composition.

Metal film resistors have heretofore been produced by the decomposition of organic palladium compounds such as palladium resinates. In view of the high specific conductivity of metallic palladium, such metallic film resistors not only needed to be extremely thin, but the resistance paths had to be extended by spiralling or printing long, narrow films to obtain a relatively high resistance of 1000 ohms or more. Such thin extended metallic films were easily damaged by handling to alter the desired resistance thereof.

It is also well established that films of good conductivity in the range of an ohm per square are obtainable

with finely divided silver fused on a ceramic surface with a glass binder. With 60% silver based on the weight of the glass flux, the resistance is only about 2 to 10 ohms per square, and with further reduction of the silver content, the composition suddenly loses conductivity. Therefore, resistors of medium or high resistance value have not been obtainable with silver-glass flux combinations.

I have now discovered that with palladium metal powder the conductivity will disappear only in the neighborhood of 8% palladium and 92% glass flux, or when using Pd plus Ag, the conductivity will not disappear until the total content of Pd plus Ag is reduced to below 8%, and that the resistance value of films having very short paths may vary from a few ohms to several megohms. Moreover, such resistors have good reproducibility. The resistivity per square of my films is, therefore, of the order of magnitude of carbon or graphite films.

The vitreous enamel resistor compositions of this invention may be prepared by mixing the vitreous enamel flux with finely divided palladium in the proportion, by weight, of 8% to 50% palladium and 92% to 50% enamel flux. The preferred compositional range is 8% to 27% palladium and 92% to 73% enamel flux.

The vitreous enamel flux used in the production of the vitreous enamel resistor compositions of this invention may be composed of any glass frit, such as a borosilicate frit, lead borosilicate frit, cadmium, barium, calcium, or other borosilicate frit. The preparation of such frits is well known and consists, for example, in melting together boric oxide, silicon dioxide and lead oxide, cadmium oxide, or barium oxide and pouring such molten composition into water to form the frit. The batch ingredients may, of course, be any compound that will yield the desired oxides under the fusing conditions of frit production, i.e. boric oxide will be obtained from boric acid or borax, silicon dioxide will be produced from flint, lead oxide will be produced from red lead or white lead, barium oxide will be produced from barium carbonate, etc.

The coarse frit is preferably milled for 2 to 20 hours, for example, in a ball-mill with water. The frit may contain varying amounts of other oxides, such as zinc oxide, magnesium oxide, or the like. The enamel flux may be composed only of frit, but preferably between 30% and 95% of Bi_2O_3 or PbO is added to the frit to produce the flux to be mixed with the finely divided palladium. It has been found that the addition of 30% to 95% Bi_2O_3 or PbO to 70% to 5% frit will permit improved reproducibility of given resistance values in resistors prepared therefrom. Moreover, such addition will permit much greater variation of firing conditions and temperatures without altering resistance values.

The compositional limits by weight are:

Palladium powder	4 to 50%	Total of Pd and Ag—8 to 50%
Silver	0 to 40%	
Flux (frit alone or frit plus Bi_2O_3 and PbO)		50 to 92%

The preferred compositional range is:

Palladium powder	4 to 15%	Total of Pd and Ag—8 to 27%
Silver	0 to 12%	
Flux (frit or frit plus Bi_2O_3 and PbO)		92 to 73%

The finely divided palladium and ground frit to be suitable for use in the preparation of resistor compositions of this invention should have an average particle size of 0.1 to 50 microns. In order to produce accurately reproducible film resistors, it is necessary to control carefully the average particle size of the palladium and frit.

The palladium powder may be obtained by chemical precipitation or by mechanical comminution in known manner. Finely divided silver, if used, should also have an average particle similar to that of the palladium and frit.

The vitreous enamel flux and palladium powder, with or without silver powder, may be mixed in any manner, for example, in a ball-mill, and the resulting dry composition sold as such. The dry composition is, however, preferably first mixed with a liquid vehicle and sold in the form of a liquid or paste. The vehicle may vary widely in composition. Any inert liquid may be employed for this purpose, for example, water, organic solvents, with or without thickening agents, stabilizing agents, or the like, for example, methyl, ethyl, butyl, propyl or higher alcohols, the corresponding esters such as the acetates, propionates, etc., the terpenes and liquid resins, for example, pine oil, alpha-terpineol, and the like, and other liquids without limitation, the function of the liquid vehicle being mainly to form a liquid or paste of the desired consistency for application purposes. The vehicles may contain or be composed of volatile liquids to promote fast setting after application, or they may contain waxes, thermoplastic resins, or wax-like materials which are thermofluid by nature whereby the composition may be applied to a ceramic insulator while at an elevated temperature to set immediately upon contact with the ceramic base.

The ceramic dielectric base material may be comprised of any ceramic material that can withstand the firing temperature of the vitreous enamel-palladium composition. For example, glass, porcelain, refractory, barium titanate, or the like may be used.

Preferably, the ceramic insulating materials should have a smooth, substantially uniform surface structure but this is not absolutely necessary.

The resistor composition is then applied in a uniform thickness on the ceramic dielectric. This may be done by any of the application methods above disclosed. The dielectric and applied resistor composition is then dried, if necessary, to remove solvent from the vehicle and then fired in a conventional lehr or furnace at a temperature at which the enamel flux is molten, whereby the conductive material is bonded to the ceramic dielectric.

The following examples are given to illustrate certain preferred details of the invention, it being understood that the details of the examples are not to be taken as in any way limiting the invention thereto. In all of the examples the particle size of the palladium, silver and flux averaged about 1 to 2 microns. Although it is desirable to maintain the particle sizes fairly consistent to obtain good reproducible results, the actual particle sizes used are not critical.

Example I

6%, by weight, of palladium powder was mixed with 35% of a lead borosilicate glass frit obtained by melting and fritting 50% PbO, 35.4% boric acid and 14.6% SiO_2. To this mixture was added 59% of an organic vehicle consisting of beta-terepineol viscosified with ethyl cellulose.

Rectangular patterns of the above resistor composition having a pasty consistency were printed by squeegeeing through a silk screen stencil between two silver conducting elements on a low dielectric constant ceramic disc (high titania body). The resistor composition was overlapped on the silver conductors to leave a resistive area of 7 x 3 mm. The dielectric and printed resistor were then fired with a firing cycle of 20 minutes with a peak temperature of 3 minutes at 760° C. The resistance value of the fired resistor was approximately 600,000 ohms. Repeated production of fired resistors by this method yielded resistors having resistance values varying between 400,000 and 800,000 ohms.

Example II

A resistor composition was prepared in the manner disclosed in Example I using a glass flux consisting of

80% Bi_2O_3 and 20% of a lead borosilicate frit obtained by melting and fritting 73.5% PbO, 17.35% boric acid and 9.15% SiO_2. The Bi_2O_3 and lead borosilicate frit were sintered together at 650° C. for 18 minutes, crushed and comminuted in a ball-mill for 16 hours to produce the glass flux.

Using the resistor composition of this example to print and fire resistor patterns as disclosed in Example I, the resistance values varied between 1.5 and 3 megohms.

Example III

A resistor composition was prepared by mixing 6% palladium powder, 3% precipitated silver, 60% of the glass flux of Example II and 31% of the organic vehicle of Example I. This resistor composition was printed and fired as set forth in Example I to produce printed, fired resistors having an average resistance value of 58,000 ohms±18%. The average voltage coefficient at 200 volts D.C. was −1.3% and the average temperature coefficient −0.1% per ° C. from −50° C. to 105° C.

Example IV

A resistor composition was prepared by mixing 5.5% palladium powder, 2.7% precipitated silver, 8.3% silver lactate, 56.5% of the flux of Example II, and 27% of the organic vehicle of Example I.

This resistor composition was printed and fired for 10 minutes at 680° C. on low dielectric constant discs as disclosed in Example I. The printed, fired resistors had an average resistance value of 43,000 ohms±7%, a voltage coefficient at 200 volts D.C. of −2.5% and a temperature coefficient of −0.1% per degree centrigrade from −50° C. to 105° C.

Throughout the specification and claims any reference to parts, proportions, and percentages refers to parts, proportions and percentages by weight unless otherwise specified.

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to said details except as set forth in the appended claims.

I claim:

1. A vitreous enamel resistor composition adapted to be applied to and fired on a ceramic dielectric to form readily reproducible electric resistors comprising 8% to 50% finely divided palladium and 92% to 50% enamel flux.

2. A vitreous enamel resistor composition adapted to be applied to and fired on a ceramic dielectric to form readily reproducible electric resistors comprising 8% to 27% finely divided palladium and 92% to 73% enamel flux.

3. A vitreous enamel resistor composition adapted to be applied to and fired on a ceramic dielectric to form readily reproducible electric resistors comprising 4% to 50% finely divided palladium, 0% to 40% finely divided silver, and 50% to 92% finely divided enamel flux, the total of finely divided palladium and finely divided silver being between 8% and 50%.

4. A vitreous enamel resistor composition adapted to be applied to and fired on a ceramic dielectric to form readily reproducible electric resistors comprising 8% to 50% finely divided palladium and 92% to 50% enamel flux, said enamel flux composed of 30% to 95% of a metal oxide taken from the group consisting of Bi_2O_3 and PbO and 70% to 5% glass frit.

5. A vitreous enamel resistor composition as defined in claim 1 containing sufficient inert liquid vehicle to form a paste with said composition components.

6. An electrical resistor comprising a ceramic dielectric containing on the surface thereof a vitreous enamel resistor element comprising between 8% and 50%, by

weight, of finely divided palladium imbedded in a glass matrix.

7. An electrical resistor comprising a ceramic dielectric containing on the surface thereof a vitreous enamel resistor element comprising between 4% and 50%, by weight, of finely divided palladium and 0% and 40% of finely divided silver imbedded in a glass matrix, the total weight of palladium and silver being between 8% and 50%.

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